

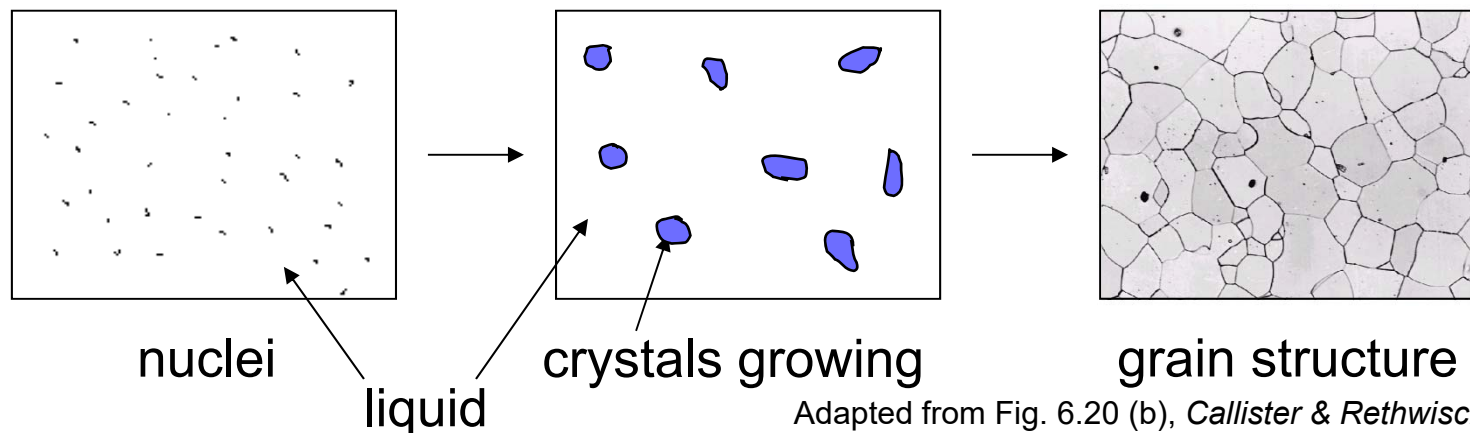
Chapter 6: Imperfections in Solids

ISSUES TO ADDRESS...

- What are the solidification mechanisms?
- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?

Imperfections in Solids

- **Solidification**- result of casting of molten material
 - 2 steps
 - Nuclei form
 - Nuclei grow to form crystals – grain structure
- Start with a molten material – all liquid

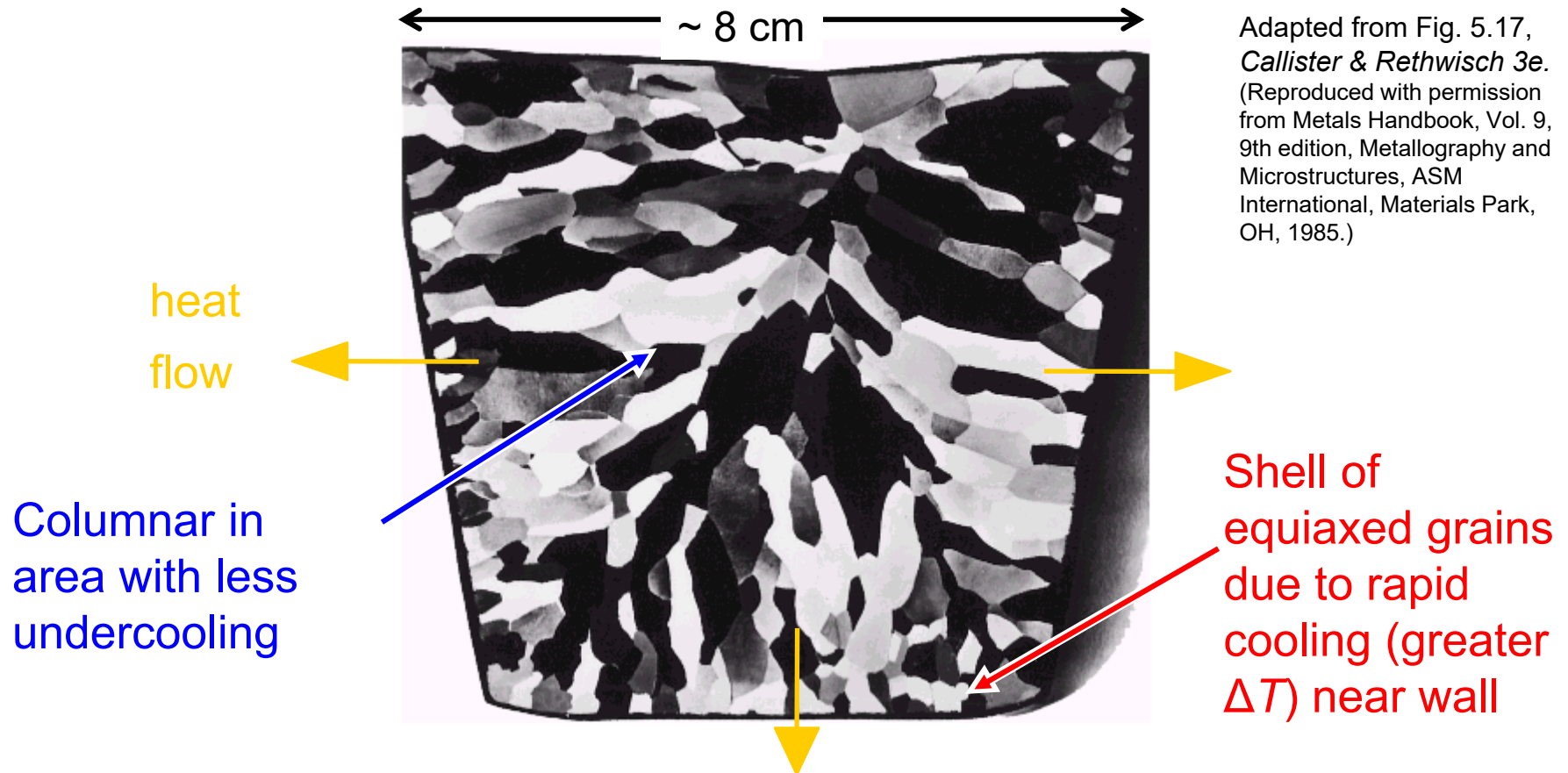


[Photomicrograph courtesy of L. C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD.)]

- Crystals grow until they meet each other

Solidification

- Grains can be
- equiaxed (roughly same size in all directions)
 - columnar (elongated grains)

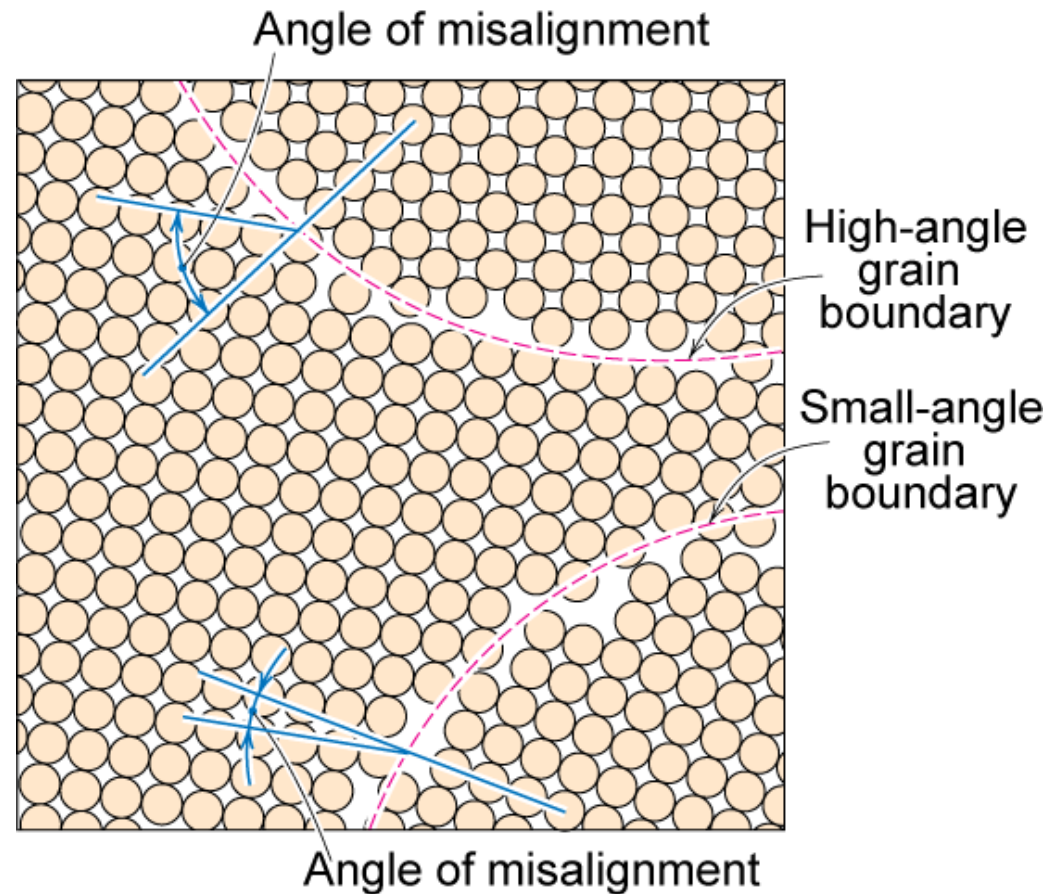


Grain Refiner - added to make smaller, more uniform, equiaxed grains.

Polycrystalline Materials

Grain Boundaries

- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
 - high mobility
 - high diffusivity
 - high chemical reactivity



Adapted from Fig. 6.14,
Callister & Rethwisch 9e.

Imperfections in Solids

There is no such thing as a perfect crystal.

- What are these imperfections?
- Why are they important?

Many of the important properties of materials are due to the presence of imperfections.

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

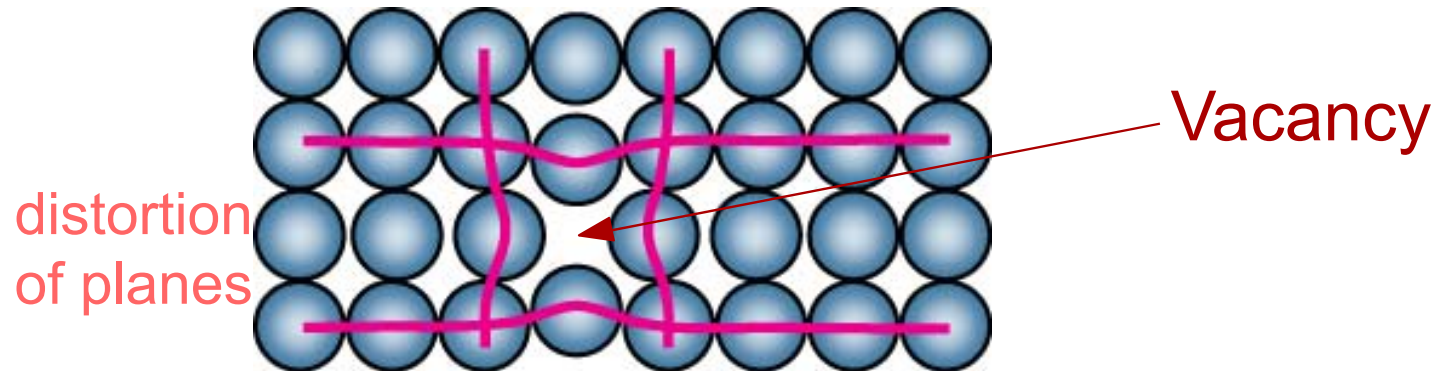
Line defects

- Grain Boundaries
- Surface

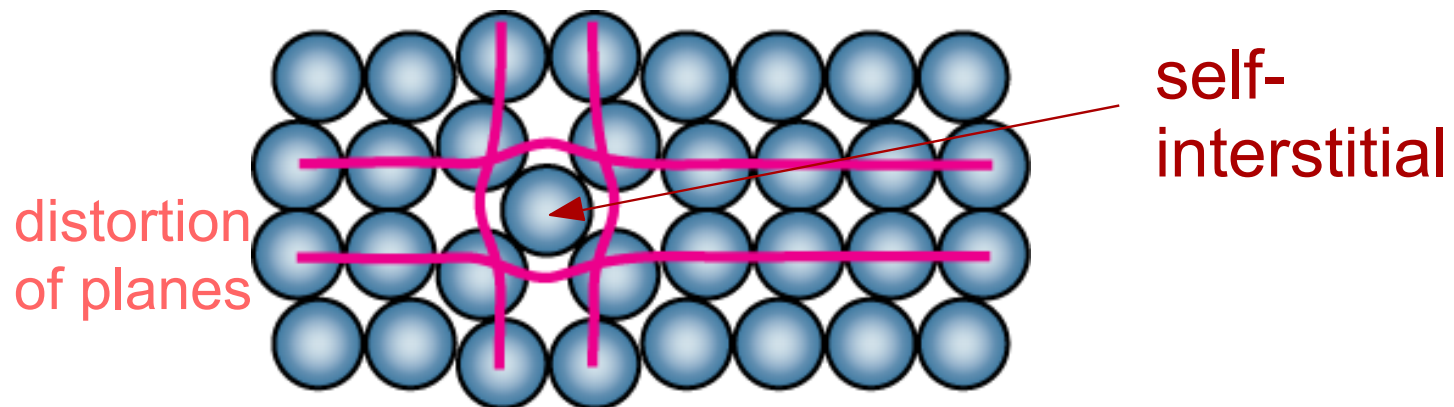
Area defects

Point Defects in Metals

- **Vacancies:**
-vacant atomic sites in a structure.



- **Self-Interstitials:**
-"extra" atoms positioned between atomic sites.



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects $\rightarrow N_v$

No. of potential defect sites $\rightarrow N$

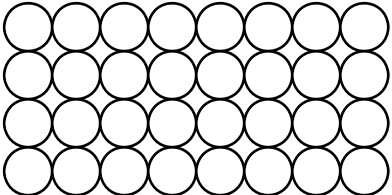
$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Activation energy $\rightarrow Q_v$

Boltzmann's constant $\rightarrow k$

Temperature $\rightarrow T$

(1.38×10^{-23} J/atom-K)
(8.62×10^{-5} eV/atom-K)



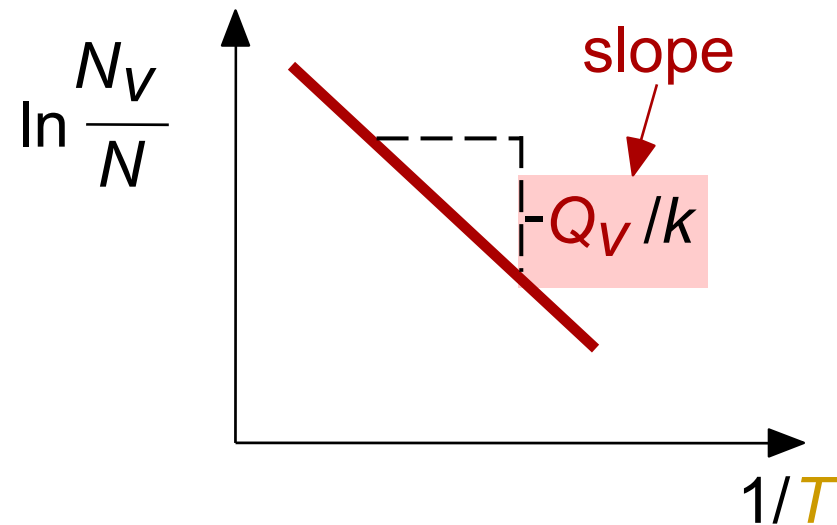
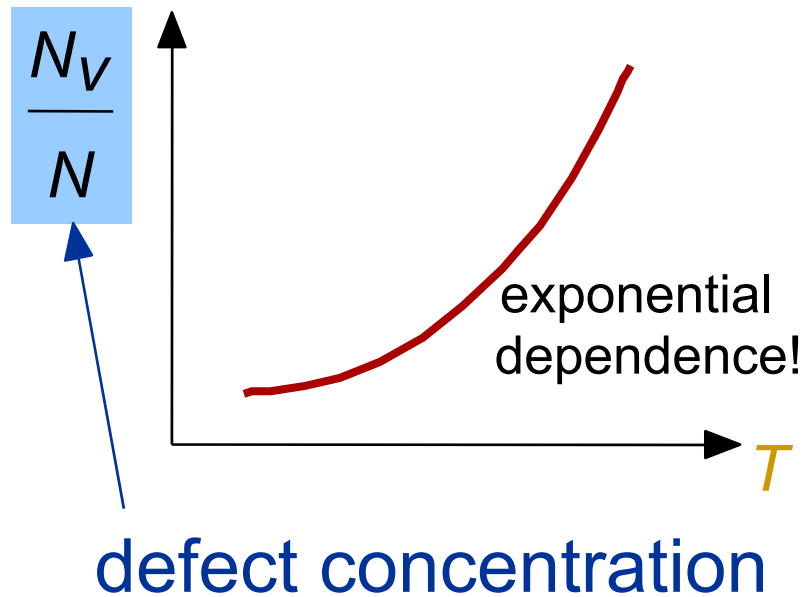
Each lattice site is a potential vacancy site

Measuring Activation Energy

- We can get Q_v from an experiment.
- Measure this...

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

- Replot it...



Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m³ of Cu at 1000°C.
- Given:

$$\rho = 8.4 \text{ g/cm}^3 \quad A_{\text{Cu}} = 63.5 \text{ g/mol}$$

$$Q_V = 0.9 \text{ eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right) = 2.7 \times 10^{-4}$$

↖ 0.9 eV/atom
↘ 1273 K
↙ 8.62 × 10⁻⁵ eV/atom-K

For 1 m³, $N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1 \text{ m}^3 = 8.0 \times 10^{28}$ sites

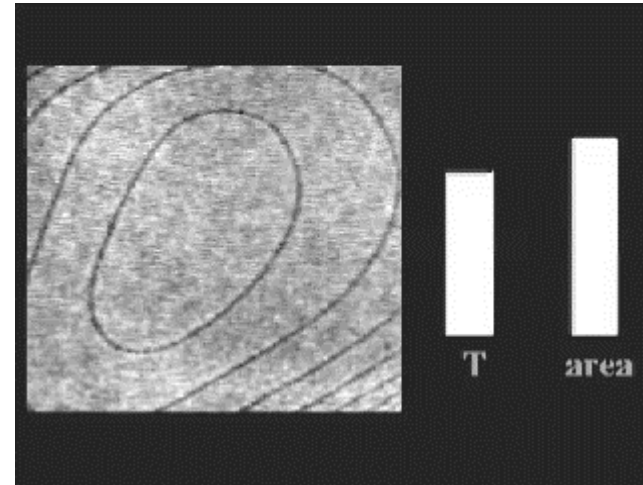
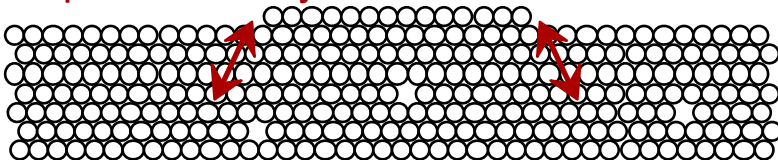
- Answer:

$$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

Observing Equilibrium Vacancy Conc.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing temperature causes surface island of atoms to grow.
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.

Island grows/shrinks to maintain equil. vacancy conc. in the bulk.



Reprinted with permission from Nature (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, Vol. 412, pp. 622-625 (2001). Image is 5.75 mm by 5.75 mm.) Copyright (2001) Macmillan Publishers, Ltd.

Point Defects in Ceramics (i)

- Vacancies
 - vacancies exist in ceramics for both cations and anions
- Interstitials
 - interstitials exist for cations
 - interstitials are not normally observed for anions because anions are large relative to the interstitial sites

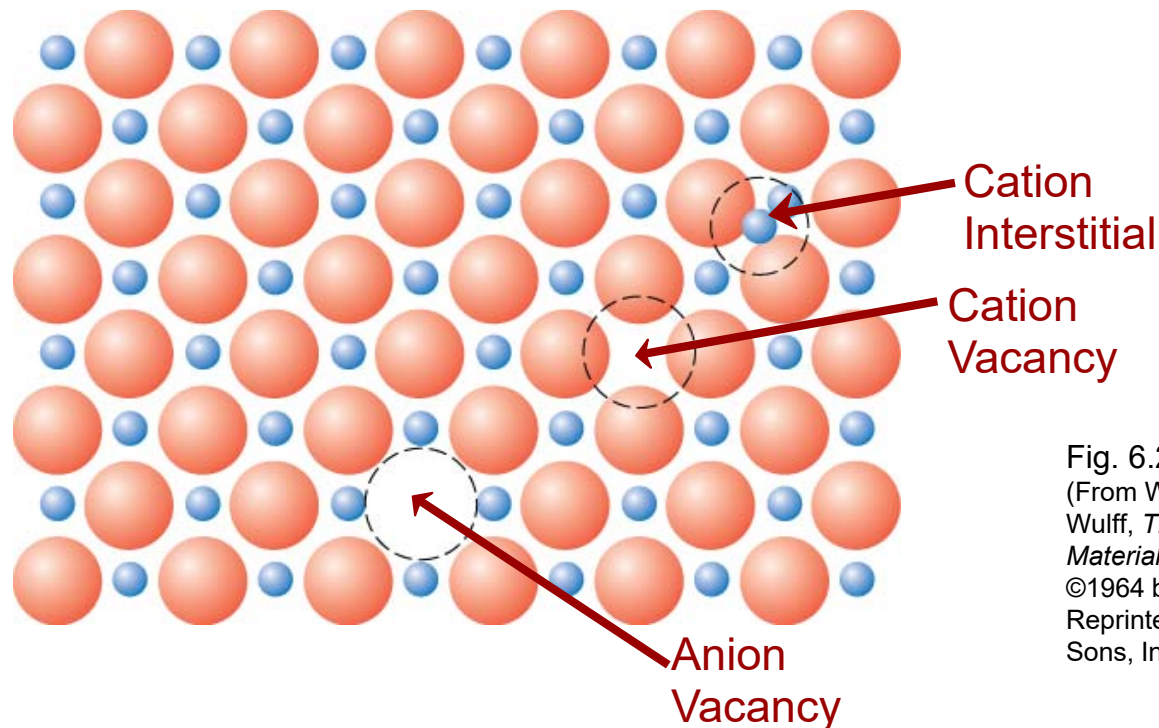


Fig. 6.2, *Callister & Rethwisch 9e*.
(From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p.78. Copyright ©1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley and Sons, Inc.)

Point Defects in Ceramics (ii)

- Frenkel Defect
 - a cation vacancy-cation interstitial pair.
- Shottky Defect
 - a paired set of cation and anion vacancies.

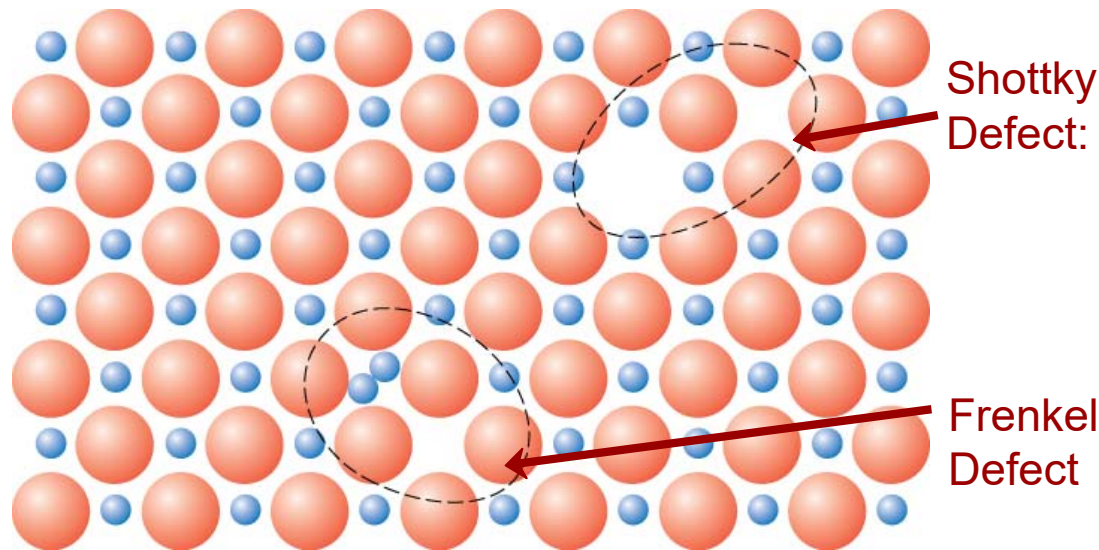


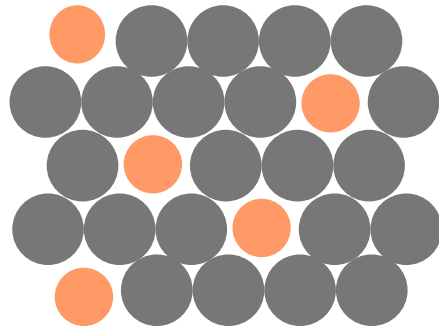
Fig. 6.3, *Callister & Rethwisch 9e*.
(From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p.78. Copyright ©1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley and Sons, Inc.)

- Equilibrium concentration of defects $\propto e^{-Q_D/kT}$

Imperfections in Metals (i)

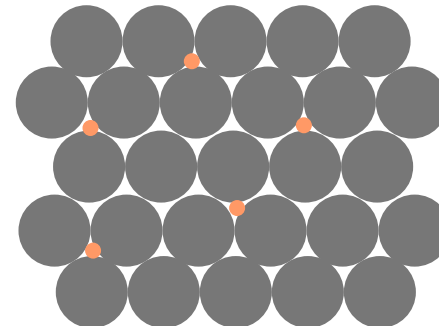
Two outcomes if impurity (B) added to host (A):

- **Solid solution** of B in A (i.e., random dist. of point defects)



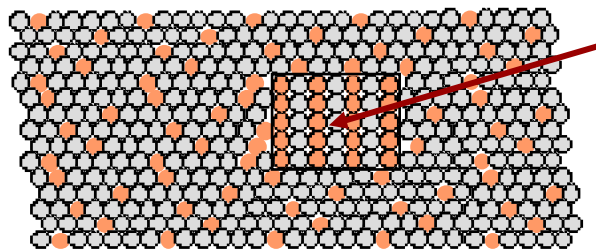
Substitutional solid soln.
(e.g., **Cu** in Ni)

OR



Interstitial solid soln.
(e.g., **C** in Fe)

- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)



Second phase particle
-- different **composition**
-- often different structure.

Imperfections in Metals (ii)

Conditions for substitutional solid solution (S.S.)

- **W. Hume – Rothery rule**
 - 1. Δr (atomic radius) < 15%
 - 2. Proximity in periodic table
 - i.e., similar electronegativities
 - 3. Same crystal structure for pure metals
 - 4. Valency
 - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

Imperfections in Metals (iii)

Application of Hume–Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

<i>Element</i>	<i>Atomic Radius (nm)</i>	<i>Crystal Structure</i>	<i>Electro-negativity</i>	<i>Valence</i>
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

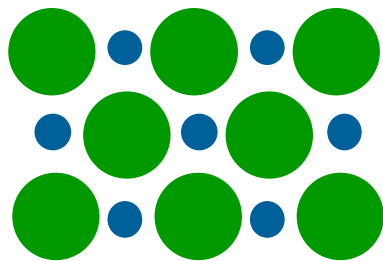
Table on p. 177, *Callister & Rethwisch 9e.*

Imperfections in Ceramics

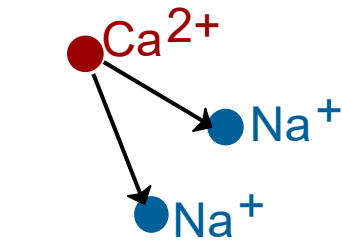
- Electroneutrality (charge balance) must be maintained when impurities are present



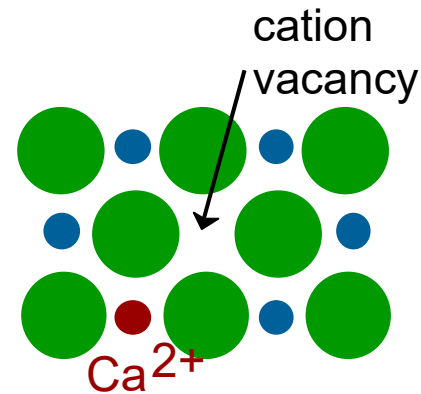
- Substitutional cation impurity



without impurity

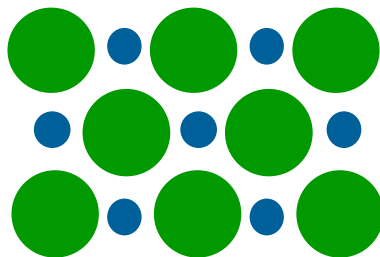


Ca^{2+} impurity

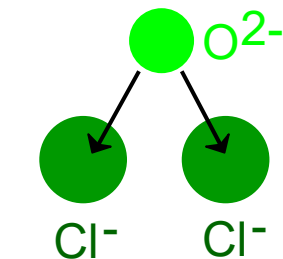


with impurity

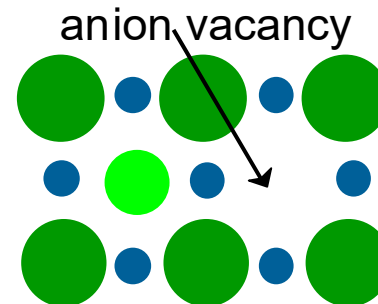
- Substitutional anion impurity



without impurity



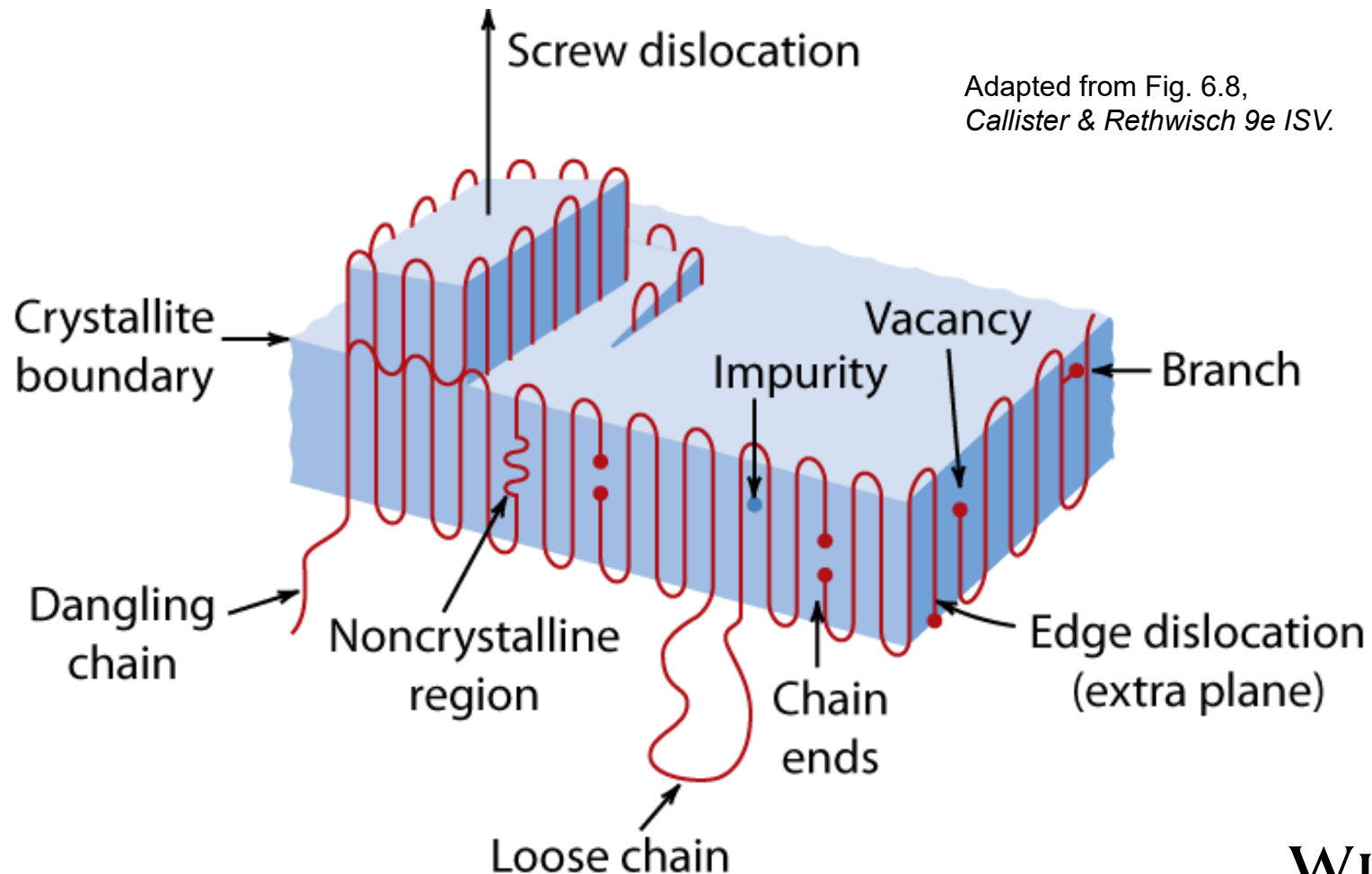
O^{2-} impurity



with impurity

Point Defects in Polymers

- Defects due in part to chain packing errors and impurities such as chain ends and side chains



Impurities in Solids

- Specification of composition

– weight percent $C_1 = \frac{m_1}{m_1 + m_2} \times 100$

m_1 = mass of component 1

– atom percent $C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$

n_{m1} = number of moles of component 1

Line Defects

Dislocations:

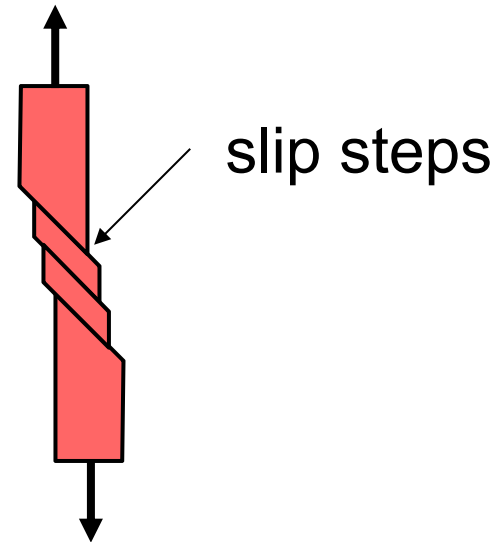
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned
- **Edge dislocation:**
 - extra half-plane of atoms inserted in a crystal structure
 - **b** perpendicular (\perp) to dislocation line
- **Screw dislocation:**
 - spiral planar ramp resulting from shear deformation
 - **b** parallel (\parallel) to dislocation line

Burger's vector, **b:** measure of lattice distortion

Imperfections in Solids

Edge Dislocation

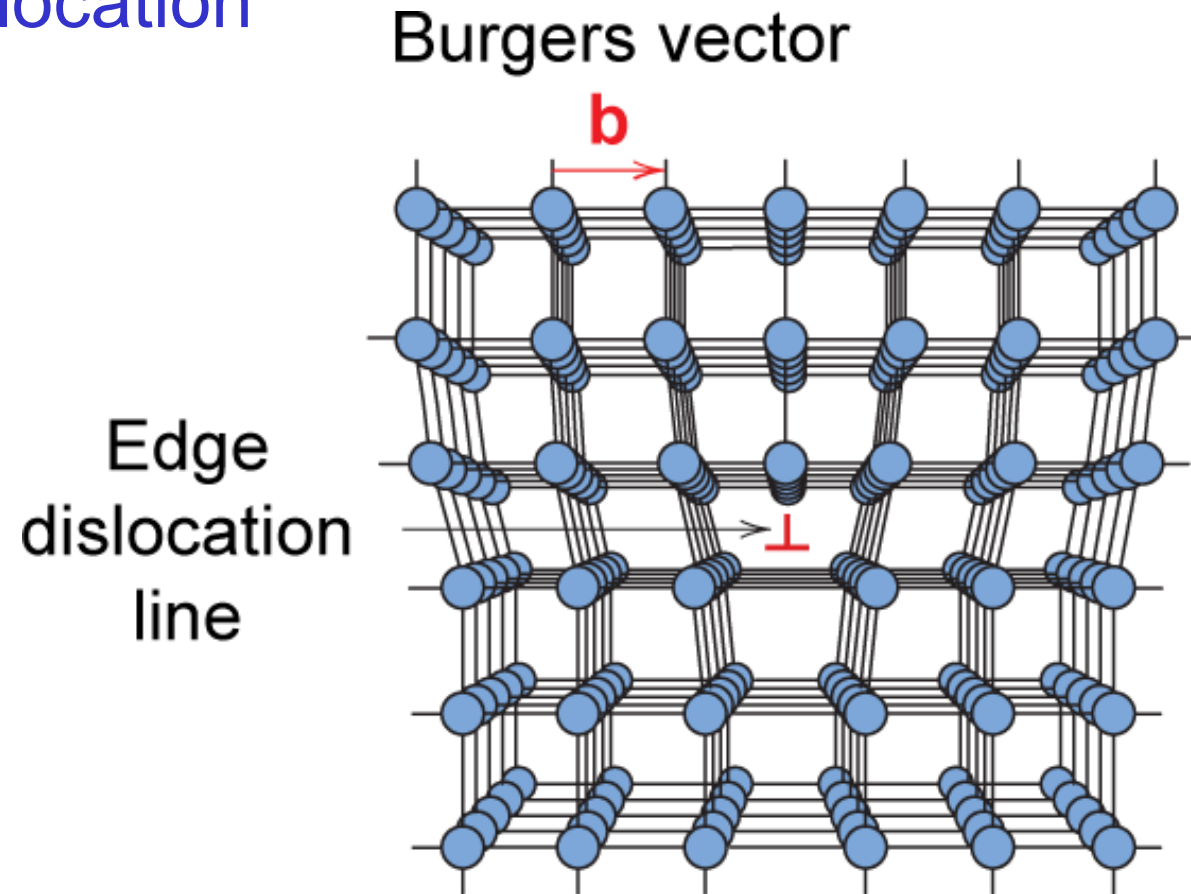
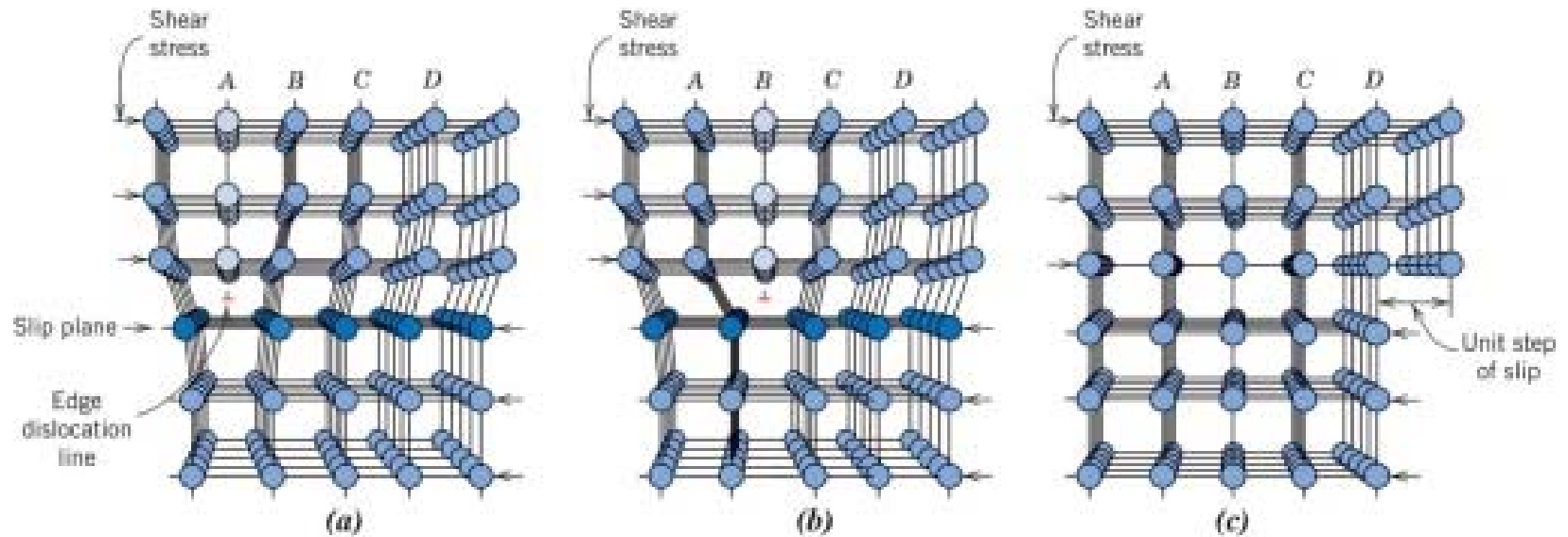
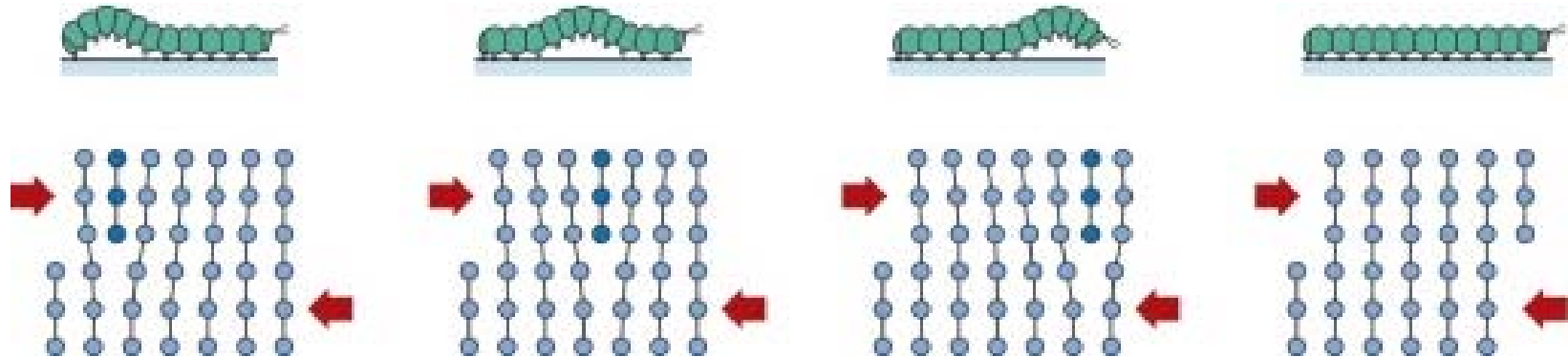


Fig. 6.9, *Callister & Rethwisch 9e*. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, NY, 1976, p. 153.)

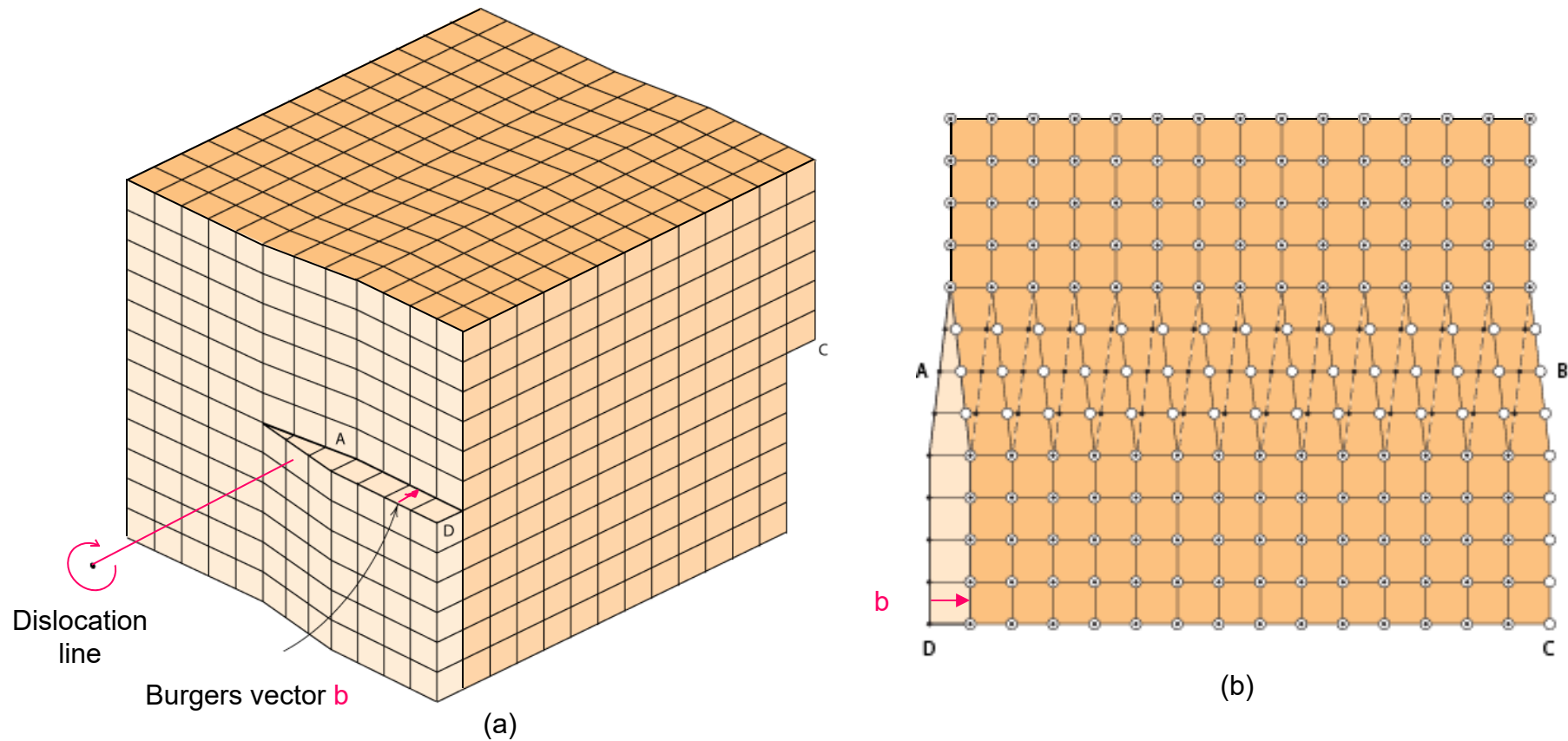


Adapted from A. G. Guy, Essentials of Materials Science, McGraw-Hill Book Company, New York, 1976, p. 153.



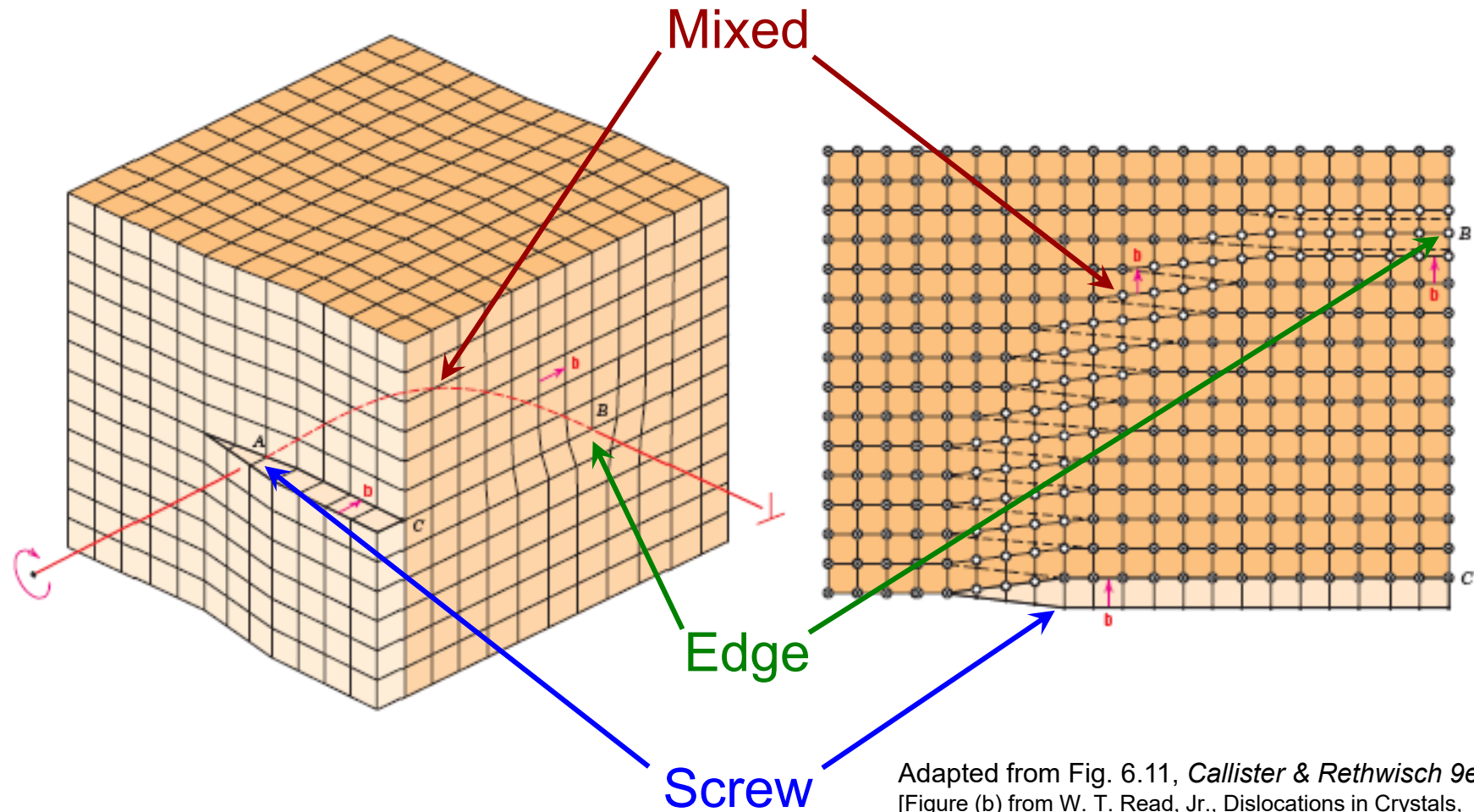
Imperfections in Solids

Screw Dislocation

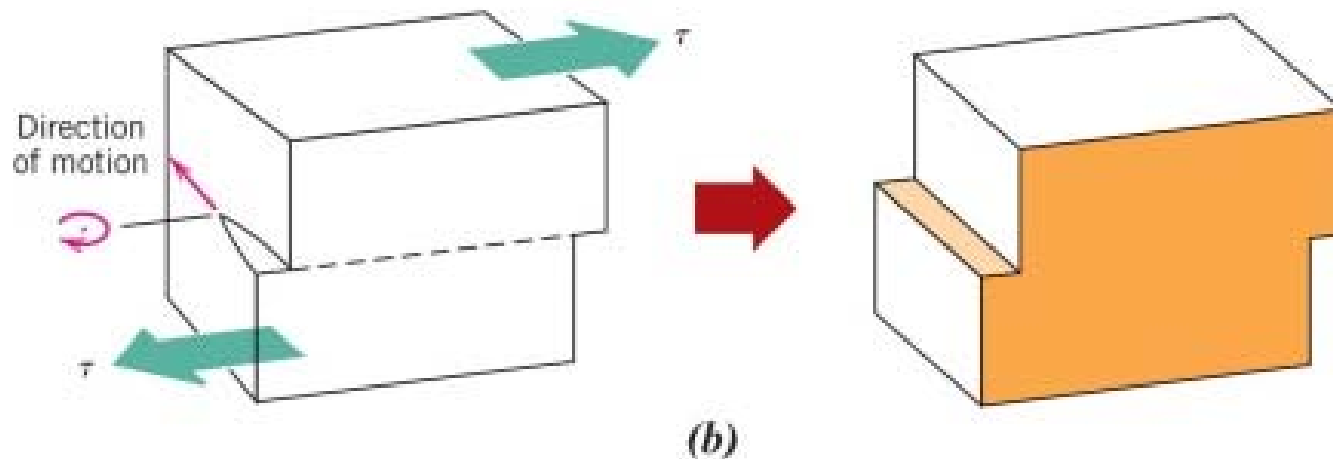
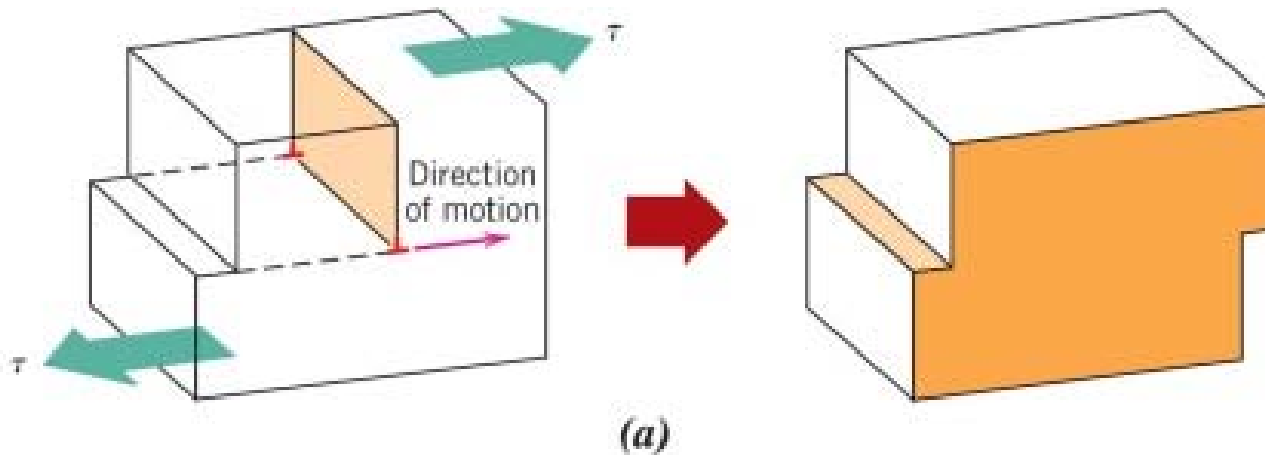


Adapted from Fig. 6.10, *Callister & Rethwisch 9e*.
[Figure (b) from W. T. Read, Jr., *Dislocations in Crystals*,
McGraw-Hill Book Company, New York, NY, 1953.]

Edge, Screw, and Mixed Dislocations



Adapted from Fig. 6.11, *Callister & Rethwisch 9e*.
[Figure (b) from W. T. Read, Jr., *Dislocations in Crystals*,
McGraw-Hill Book Company, New York, NY, 1953.]



Adapted from H. W. Hayden, W. G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, Mechanical Behavior, p. 70. Copyright © 1965 by John Wiley & Sons, New York.

Imperfections in Solids

Dislocations are visible in electron micrographs

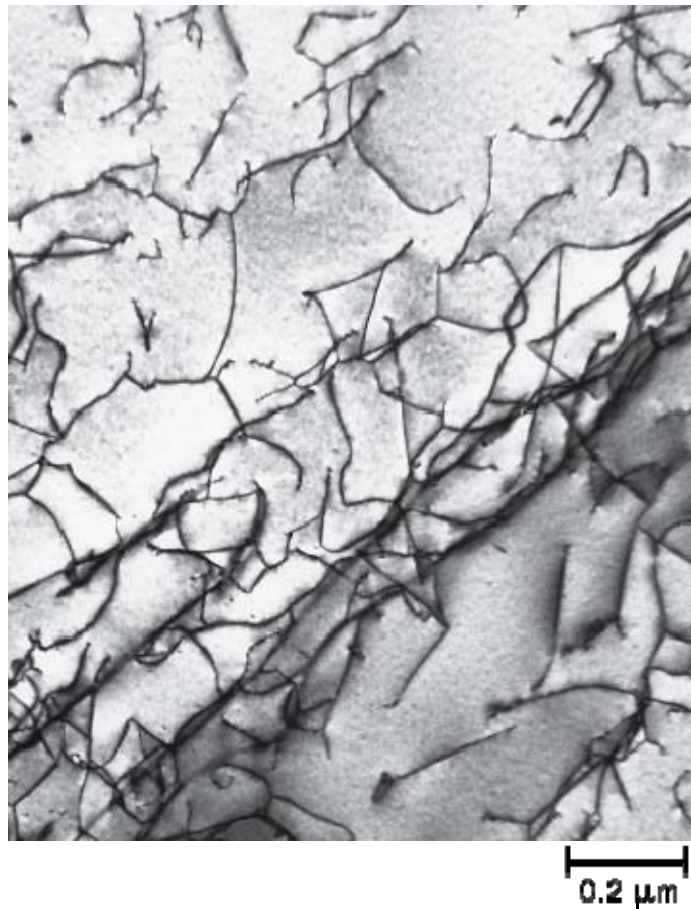
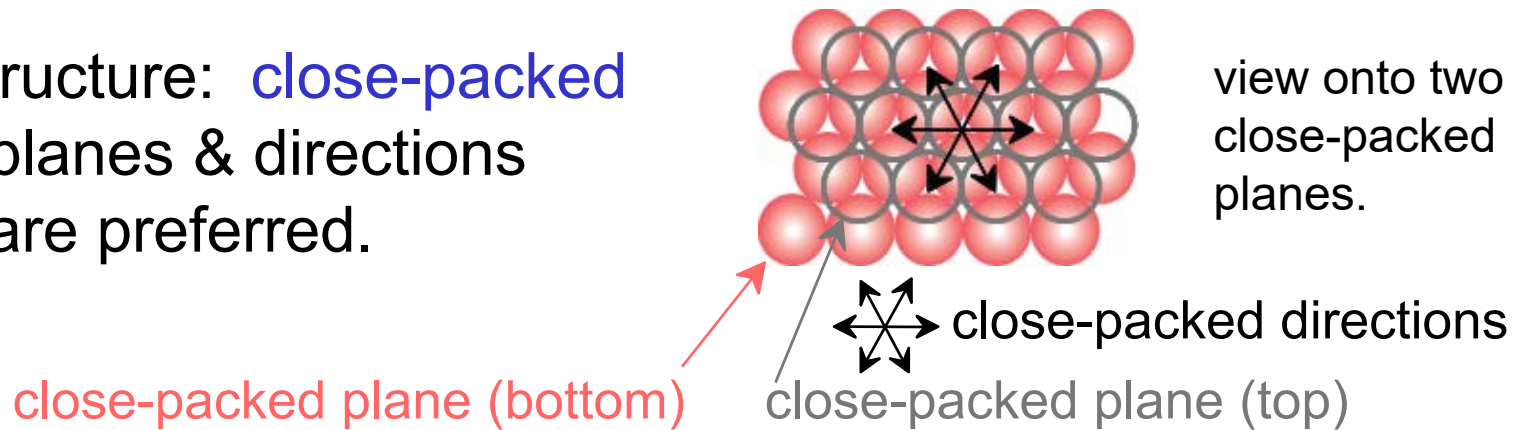


Fig. 6.12, *Callister & Rethwisch 9e*.
(Courtesy of M. R. Plichta, Michigan
Technological University.)

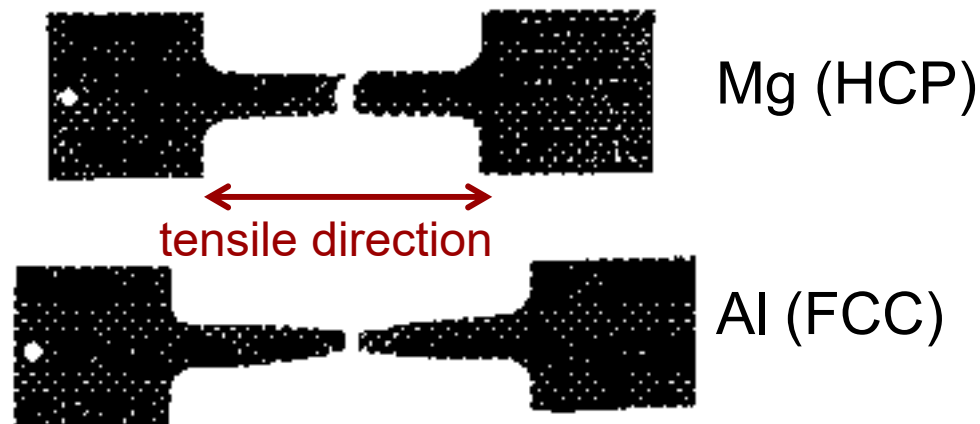
Dislocations & Crystal Structures

- Structure: **close-packed** planes & directions are preferred.



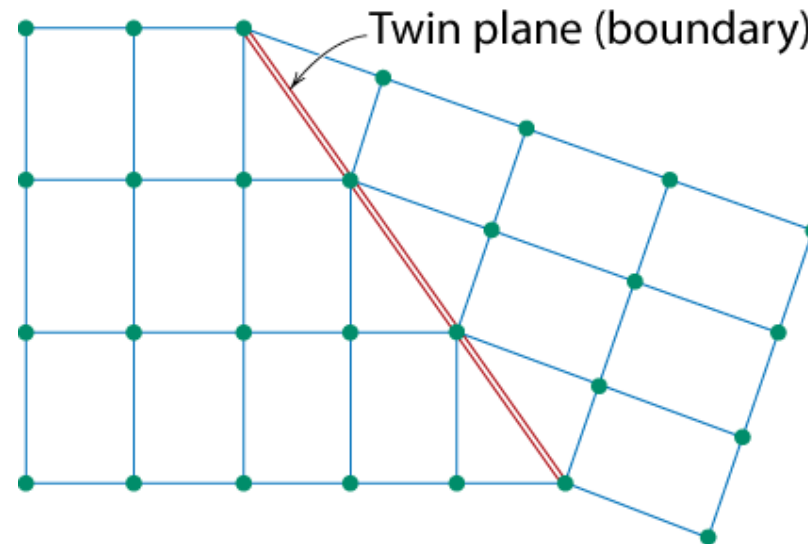
- Comparison among crystal structures:
FCC: many close-packed planes/directions;
HCP: only one plane, 3 directions;
BCC: none

- Specimens that were tensile tested.



Planar Defects in Solids

- One case is a **twin boundary (plane)**
 - Essentially a reflection of atom positions across the **twin plane**.



Adapted from Fig. 6.15,
Callister & Rethwisch 9e.

- **Stacking faults**
 - For FCC metals an error in ABCABC packing sequence
 - Ex: ABCABABC

Catalysts and Surface Defects

- A **catalyst** increases the rate of a chemical reaction without being consumed
- Active sites on catalysts are normally surface defects

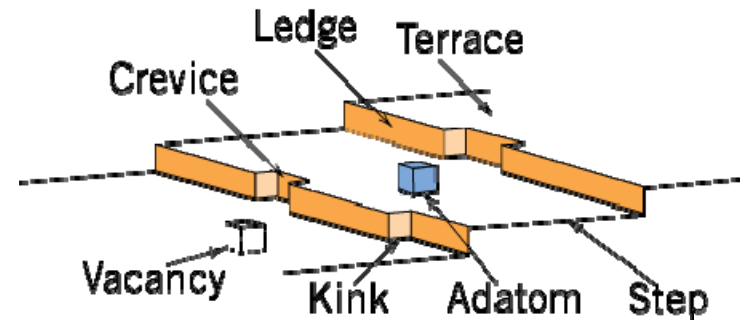
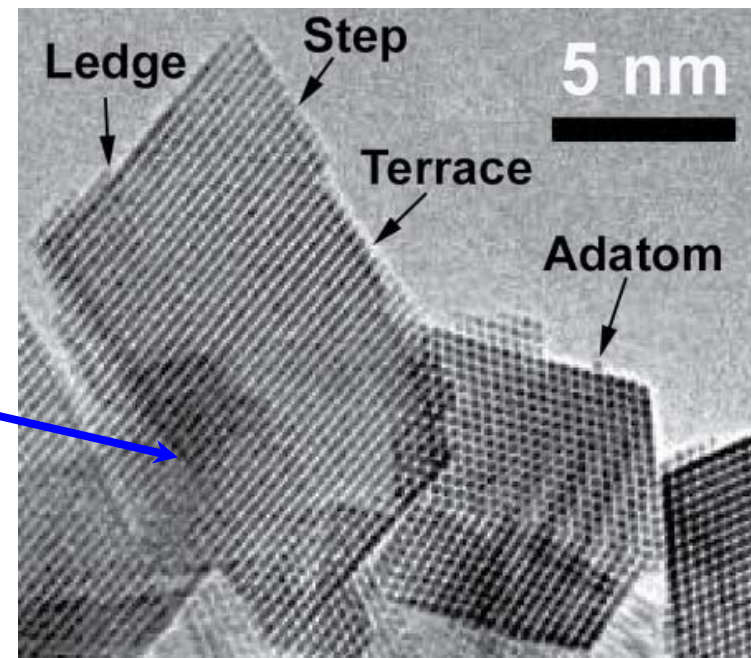


Fig. 6.16, Callister & Rethwisch 9e.

Single crystals of $(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2$ used in an automotive catalytic converter

Fig. 6.17, Callister & Rethwisch 9e.



Microscopic Examination

- Crystallites (grains) and grain boundaries. Vary considerably in size. Can be quite large.
 - ex: Large single crystal of quartz or diamond or Si
 - ex: Aluminum light post or garbage can - see the individual grains
- Crystallites (grains) can be quite small (mm or less) – necessary to observe with a microscope.

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.

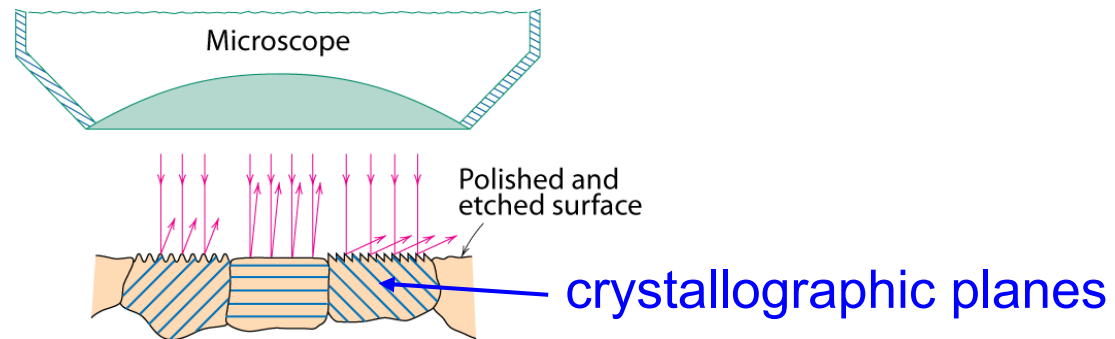
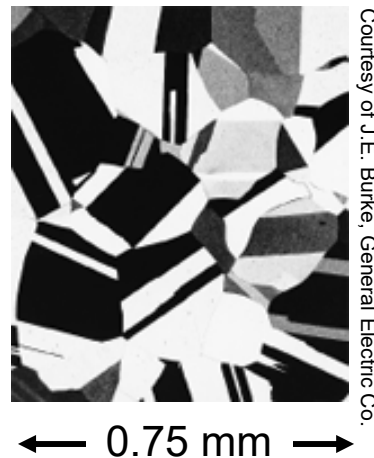


Fig. 6.19(b) & (c), Callister & Rethwisch 9e.



Courtesy of J.E. Burke, General Electric Co.

Micrograph of brass (a Cu-Zn alloy)

Optical Microscopy

Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

ASTM grain size number

$$N = 2^{n-1}$$

number of grains/in²
at 100x
magnification

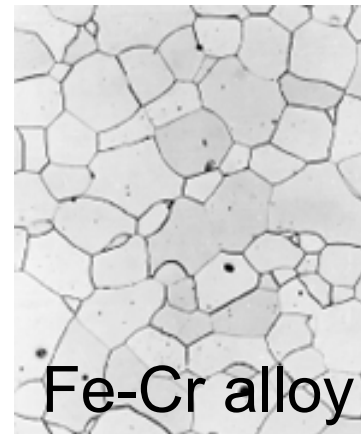
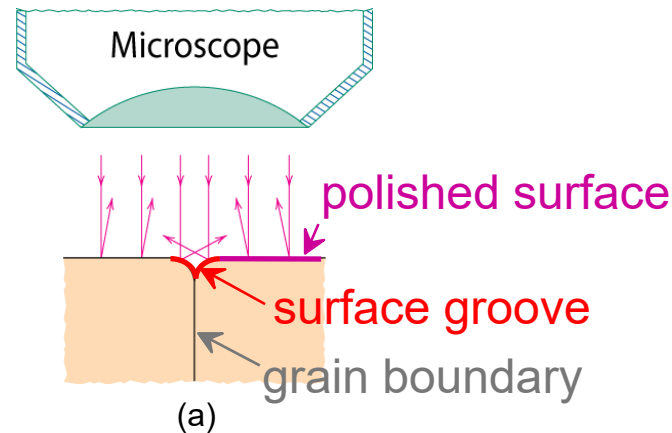


Fig. 6.20(a) & (b), *Callister & Rethwisch 9e*.

[Fig. 6.20(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

Microscopy

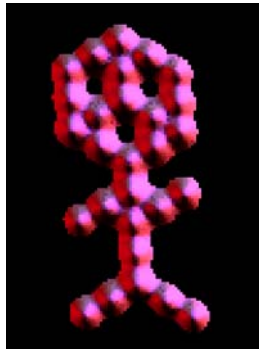
Optical resolution ca. 10^{-7} m = 0.1 μ m = 100 nm

For higher resolution need higher frequency

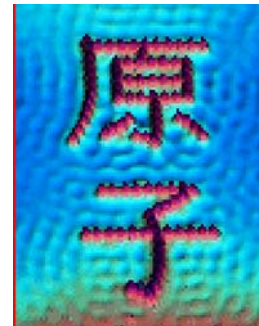
- X-Rays? Difficult to focus.
- Electrons
 - wavelengths ca. 3 pm (0.003 nm)
 - (Magnification - 1,000,000X)
 - Atomic resolution possible
 - Electron beam focused by magnetic lenses.

Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!



Carbon monoxide molecules arranged on a platinum (111) surface.



Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word "atom".

Photos produced from the work of C.P. Lutz, Zeppenfeld, and D.M. Eigler. Reprinted with permission from International Business Machines Corporation, copyright 1995.

Summary

- Point, Line, and Area defects exist in solids.
- The number and type of defects can be varied and controlled (e.g., temperature controls vacancy concentration).
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not).